

# Relativistic Configuration Interaction Fe III $3d^6$ $J=4 \rightarrow 3d^5 4p$ $J=3,4,5$ $f$ -values

**Donald R. Beck**

Physics Department, Michigan Technological University, Houghton, MI 49931-1295,  
USA

**Abstract.**

Electric Dipole  $f$ -values have been obtained between the seven  $3d^6$   $J=4$  even states, and all the  $3d^5 4p$   $J=3,4,5$  odd states. Seventy two of these exceed 0.01 and are published here. The average agreement between the length and velocity gauges is 1.8%. Due to the small size of the  $f$ -values, non-orthogonality effects may be significant in shell jump cases, as we have here. Many of the odd levels are so nearly degenerate that the introduction of small semi-empirical corrections is necessary. We compare favorably (17% on average) to the most modern of the three available semi-empirical data sets.

PACS numbers: 31.25.Eb, 31.25.Jf, 32.10.Fn, 32.70.Cs

## 1. Introduction

Oscillator strengths of Fe ions are of great interest to astrophysicists [1], but there is still a paucity of both *ab initio* and experimental results for the lightly ionized species. Fe II ions, for example, have been recently used in the astrophysical search of the possible time variation of the fine structure constant [2]. On the other hand, for the ion of interest here, Fe III, and Fe II which we previously studied [3, 4], there are three extensive semi-empirical data sets [5-7].

The difficulty in treating these ions from an *ab initio* perspective is several fold: (1) relativistic effects must be incorporated to account for the proper relative positioning of  $3d^{n-1}4s$ ,  $3d^n$  and/or  $3d^{n-2}4s^2$  energy levels which may be nearly degenerate. This is because relativistic effects for 4s and 3d electrons differ by  $\sim 0.1$  eV [8], (2) the most nearly degenerate levels (say  $< 250$   $\text{cm}^{-1}$ ) are so close as to make it very difficult to position them in a purely *ab initio* manner, and thus some additional procedure, such as “fine tuning” [9] may become necessary. Accurate positioning of nearly degenerate levels can be essential to producing proper mixing of basis functions, so necessary to generating reliable  $f$ -values, (3) the presence of so many (5 or 6, here) open shell  $d$  electrons requires the use of goodly number of complicated  $N$ -electron basis functions which require sophisticated efficient computer algorithms to deal with them.

Despite these concerns, relativistic configuration interaction (RCI) treatments of bound state properties of  $(3d+4s)^n$  states are becoming quite capable of delivering accurate results for the entire observed [10] bound state spectrum. Beyond the interest to the astrophysical community, work on these ions serves to extend and make more efficient the computer algorithms involved [3,9,11,12].

## 2. Methodology

The Hamiltonian used to generate the radial function is the Dirac-Coulomb one with a uniform charge distribution nuclear model. Magnetic Breit effects are inserted in the later stages of the Relativistic Configuration Interaction (RCI) calculations.

In RCI, the wavefunctions are eigenstates of  $J^2$ ,  $J_z$  and parity, and are separated into a reference and a correlation part. Usually, the reference part consists of the single non-relativistic manifold ( $3d^6$  and  $3d^5 4p$ , here) that dominates the levels of interest. All reference radial functions are determined numerically by solving the Dirac-Fock-Coulomb equations using Desclaux’s algorithm [13] for the lowest energy level. Sometimes a radial function, e.g.  $4p_{1/2}$  in  $3d^5$  (“ $^6S$ ”)  $4p J=4$ , is “nearly” absent from this energy level, and a “spurious” radial function ( $4p_{1/2}$ ) may be generated. This problem is removed by generating the  $4p_{1/2}$  from a low-lying excited level, e.g.  $3d^5$  (“ $^4G$ ”)  $4p J=4$ , for which it does make a substantial contribution. The remaining variation of the outer radials is accounted for at the correlation stage, through the inclusion of manifolds like  $3d^5 vp$ . Here,  $vp$  is a radial determined during the RCI process, which is represented by a relativistic screened hydrogenic (RSH) function. The screening constant ( $Z^*$ ) is

estimated by matching the virtual's  $\langle r \rangle$  to that of the reference radial it is replacing. The final value of  $Z^*$  is determined during the RCI process (energy variational principle). Finally, the two particle electrostatic radial integral coefficient's contribution to the structure, required by the Desclaux version we are using [13], is created by our RCI program [12].

For ease of analysis, and introduction of the small semi-empirical shifts, the  $|jjJJ_z\rangle$  reference basis functions are rotated to a  $|“SL”JJ_z\rangle$  basis during the RCI process, with no loss of completeness. This is done by neglecting the minor radial component, and assuming the major radial component doesn't depend on  $j$ , and diagonalizing the  $L^2 + A * S^2$  matrix ( $A$  is chosen to separate  $L^2$  and  $S^2$  eigenvalues). While this in principle can be done for all the correlation functions too, it is expensive, and also unnecessary.

To introduce correlation, we apply perturbation theory to suggest what additional manifolds are needed in the wavefunctions. Here, single and double excitations from the outer subshells (3s, 3p, 3d, 4p) suffice [3]. The additional radial functions needed (the “virtuals”) represent the compact portion of an entire Rydberg and continuum series, and  $\sim 2$  per symmetry ( $\kappa$ )/shell are sufficient to capture  $\sim 90\%$  of the correlation energy. Virtual orbital symmetries higher than  $l=5$  contribute  $< 100 \text{ cm}^{-1}$  to energy differences and are not included [3]. Each reference function is “equivalently” correlated, i.e. has the same single and pair excitations (e.g.  $3d^2 \rightarrow vf^2$ ) generated from it.

It is important to have some systematic way of making sure adequate radial and angular convergence has been achieved. Past non-relativistic work on light atoms has shown [14] that the total “bi-virtual” correlation energy can be expressed as a sum of products of group theoretical factors ( $\beta$ 's) and radial pair energies ( $\epsilon$ 's). For low  $Z$  atoms, it was found that the  $\epsilon$ 's were fairly invariant to  $Z$  and ionization stages [14]. With the  $\beta$ 's known [15], the  $\epsilon$ 's can be extracted from a much simpler (e.g. all closed subshells, as for Zn III [16]) system with a similar  $Z$ . These then can be used with the  $\beta$ 's for the Fe III states of interest to provide an estimate, pair-by-pair, of the amount of correlation energy our RCI calculation should be producing. This procedure has been found to work well for both transition metal and lanthanide atoms [4].

Sometimes it is not possible to include enough correlation to adequately position levels, and the prediction of properties is insufficiently accurate. Missing correlation tends to fall into two categories: (1) that missing from “nearby” single excitations, such as  $3d^5(5p+4f)$  and  $3d^4 4s 4p$ . An example would be  $3p^2 \rightarrow 3d^2$  from  $3d^5 5p$  which would be a triple excitation from our  $3d^5 4p$  reference manifold. Triple (and quadruple) excitations can be expensive to include, and a cruder treatment is often more efficient and still satisfactory. This is to simply shift the diagonal matrix elements of the singles (e.g.  $3d^5 5p$ ) down by the amount of correlation energy included in the  $3s^2 3p^6 3d^5$  core of  $3d^5 4p$ . In the present instance, this is about  $-0.2$  a.u. An earlier study [3] showed that this was an effective way to replace the inclusion of triples; viz as individual large triples were included, the shift was reduced by the amount of correlation energy the triple contributed to e.g.  $3d^5 5p$  without changing the wavefunctions of the  $3d^5 4p$  levels

below  $3d^5 5p$  in a significant way. In the odd parity cases examined here, there are a few  $3d^5 4p$  levels above [10]  $3d^5(5p+4f)$  and  $3d^4 4s 4p$ , but we do not present results for these. Too little is gained for too much effort, and the positions of these  $3d^5 4p$  levels are already known [5].

The remaining few shifts of order  $2\text{-}300\text{ cm}^{-1}$  are within  $3d^5 4p$  and are done to adjust the positions of nearly degenerate levels arising from differing  $3d^5$  “LS” parents. This is likely the less well converged part of the correlation energy. Here, in a few cases, we are trying to bring results into conformity with observed energies [5, 10] and the “label” given to the levels. These “labels” however are not measured, but a product of semi-empirical fitting of the energy levels [5-7] using a limited basis, including scaling. While this procedure has had considerable success in complicated cases, it should be of future interest in semi-empirical work to provide an estimate of how the “fitting quality” varies if the identity of two (or more) nearly degenerate levels (say within  $200\text{ cm}^{-1}$ ) is “flipped”. A more rigorous “test” would be to have experimentally determined Landé  $g$ -values for each of the levels, but unfortunately these are not available for Fe III.

In the next section, we discuss the results obtained for the Fe III  $J=3,4,5$  (odd) energies and wavefunctions. The Fe III  $J=4$  energies and wavefunctions have been discussed previously [3,4] and are thus not included here. In diagonalizing the RCI matrix, it was necessary to make a small technical improvement in the diagonalizer we use [17]. Initially, for the uppermost  $J=3,4$  (odd)  $3d^5 4p$  levels, convergence failures were observed. This problem was removed by increasing the size (from 120 to 200) of the small matrix used during the iteration process [17]. The remaining section deals with the reported  $f$ -values—how they were computed, the role of non-orthogonality, gauge agreements, and comparison with semi-empirical results.

### 3. Results

#### 3.1. Fe III $J=3,4,5$ (odd) Energy Levels

The results for the lowest 43 of 46, 36 of 37, and 24 of 24  $J=3,4,5$  levels are given in Tables 1, 2 and 3 respectively. The most important direct measure of accuracy, we feel, is how well we account for the splitting between adjacent energy levels (particularly the nearly degenerate ones) as this should give a good measure as to the correctness of the mixing of the  $3d^5 4p$  basis functions into the the RCI eigenvectors. For  $J=3,4,5$  the magnitude of the average adjacent error is  $193\text{ cm}^{-1}$ (15%),  $206\text{ cm}^{-1}$ (23%) and  $170\text{ cm}^{-1}$ (15%) respectively. The fact that fairly small errors in energy differences give rise to moderate sized percentage errors is an indication of the significant amount of near degeneracy associated with the levels. These percentage errors mainly arise from adjacent levels exhibiting a high degree of near degeneracy. Labels for such levels (first and last columns of the Tables) are the least certain. The impact of this on  $f$ -values is discussed in the next section.

The results in these tables were obtained using basis sets having 10816, 11839 and

12600 members for  $J=3, 4, 5$  respectively. These sets have been considerably compressed using our REDUCE procedure [3,12]. Its essence is to rotate the original basis set to maximize the number of zero interactions with the reference space, and discard the rotated basis functions producing a zero interaction. Energy losses are well below  $100 \text{ cm}^{-1}$ . To illustrate the reduction, for  $J=3$  (odd) the pair correlation  $3d^2 \rightarrow vf^2$  produces 1026 basis functions, which REDUCE rotates to 138 ( $46 \times 3$ ) which we keep.

In Tables 1-3, the label in the first column is taken from ref. [10], and its percentage weight is the first number in the last column. Many of the levels are so impure (other labels with weights  $> 10\%$ ) that additional labels need to be specified. Sometimes one (or more) of these “secondary” labels should really be used to label the state. We have also included RCI values of the Landé  $g$  values in Tables 1-3.

### 3.2. $f$ -values

Our  $f$ -values are computed in the length and velocity gauges, using the experimental energy differences [10] and include the effects of non-orthogonality (NON). For the moderate ( $.01 < f < .10$ ) shell jump ( $3d^6 \rightarrow 3d^5 4p$ ) transitions presented here in Tables 4-6, NON effects may be significant. For example, a  $\langle 3d|r|4p \rangle$  radial transition integral is of order  $10^{-4}$  whereas a  $\langle 3d|r|3p \rangle$  radial transition integral is of order  $10^{-2}$ . The latter is pre-multiplied (in the first order NON correction) by the radial overlap integral  $\langle 3p|4p \rangle$  which is of order  $10^{-2}$ . Thus, in the absence of angular factors, the “lead” term and the first order NON correction are of the same magnitude.

A direct calculation with no correlation for the  $a^5D \rightarrow (a^4G) z^5F_5$  transition gives  $(f_v, f_l) = (.118, .113)$  with NON, and  $= (.134, .075)$  without NON. The “without” calculation is done using the reference radials of  $3d^5 4p$  for the radial sets of both states ( $^5D, ^5F_5$ ). For reference (see Table 6) the RCI values, which include correlation,  $= (.103, .0957)$ . NON exists in our calculations because the even and odd parity states are obtained totally independently.

The average gauge agreement for all 72 transitions in Tables 4-6 is 1.8%, low for RCI results. Agreement with the semi-empirical results is good—the best for the Raassen values [7] (19%), followed by Ekberg [5] (24%) and Kurucz [6] (30%). For  $a^5D_4 \rightarrow z^5P_3$ , there is an *ab initio* value available [9] of .0596 which lies between our two RCI gauge results (Table 4).

There are a few notable discrepancies between RCI and the semi-empirical results in Tables 4-6. Some of these are associated with transitions to nearly degenerate levels about which there are “labelling” differences—for example  $w^3G$  and  $y^3I$  of  $J=5$  (odd). Here the comparison is best made between the sum of the two  $f$ -values (e.g.  $^3F \rightarrow w^3G + y^3I$ ). Indeed the agreement is better for the sum (it is the sum which is used to determine the “agreement” percentage). It has been formally shown [18] that the sum of  $f$ -values to nearly degenerate levels (from a single origin) should be approximately constant, independent of the precise mixing of the two (or more) dominant basis functions. Improved accuracy for individual transitions within the sum

might be achieved using measured Landé  $g$ -values and/or much more strenuous *ab initio* calculations.

There are a few transitions for which Ekberg [5] is quite different from both RCI and Raassen [7], viz  $a^1G \rightarrow (a^2G) v^3F_{3,4}^o + (a^2G) y^1H_5^o$  and  $b^1G \rightarrow (b^2G) w^1H_5^o$ . It is mainly these few values which reduce our agreement (from the “Raassen level”).

#### 4. Summary

The seventy two  $f$ -values exceeding .01 have been tabulated for Fe III electric dipole transitions between  $3d^6 J=4$  and  $3d^54p J=3,4,5$  states. The average agreement between the velocity and length gauges is 1.8%, and the average agreement with the semi-empirical data base values of Raassen [7] is 19%.

Labelling of several nearly degenerate odd parity levels is still somewhat uncertain, and would benefit from experimental determination of Landé  $g$ -values for them. Although the sum of  $f$ -values to such levels from a single even parity level is stable as might be expected [18], i.e. nearly independent of labelling (“flipping”), the future availability of experimental  $f$ -values would be helpful here also. It might also be useful if future semi-empirical results included an estimate of how the rms fit to observed energy levels is impacted by “flipping” in such nearly degenerate cases.

Our numerical radial functions for the reference configuration(s) are normally generated [13] by optimizing on the lowest root. However, sometimes a radial function (e. g.  $4p_{1/2}$ ) makes little or no contribution to this wavefunction, and a spurious ( $4p_{1/2}$ ) radial function may be generated. Here, we remove this problem by generating the  $4p_{1/2}$  radial function from a low excited state, for which it does make a significant contribution. In this work, we sometimes found the diagonalizer had trouble converging for some of the highest excited states (e.g. in the top 10 or so out of 60). We overcame this by increasing the size of the small matrix (from order 120 to 200) used during the iteration process [17]. Finally, we note that for some of the shell jump ( $3d \rightarrow 4p$ )  $f$ -values here, inclusion of non-orthogonality effects can be important (if the odd and even parity wavefunctions are computed with different radial basis sets, as we do). This warns us that it is not always possible to limit such effects to neutral atoms and first ions [19].

#### Acknowledgments

We thank our referees for the helpful comments they have made in improving the text. Support from the National Science Foundation, Grant No. PHY-0097111 is gratefully acknowledged.

#### References

- [1] Johansson S *et al*, in *Proc. 7th International Colloquium on Atomic Spectra and Oscillator Strengths* (edited by Hibbert A and Wiese W L) 2002 *Phys. Scr.* **T100** 71

- [2] Levshakov S A *et al* 2006 *Astron. Astrophys.* **449** 879 and references therein
- [3] Beck D R 2005 *Phys. Scr.* **71** 447
- [4] Beck D R 2007 *J. Phys. B.* **40** 651
- [5] Ekberg J O 1993 *Astron. Astrophys. Suppl. Ser.* **101** 1
- [6] Kurucz R L online database at <http://kurucz.harvard.edu/atoms/2602/>
- [7] Raassen A J J, online database at <ftp://ftp.wins.uva.nl/pub/orth/iron/FeIII.E1> (1999)
- [8] Martin R L and Hay P J 1981 *J. Chem. Phys.* **75** 4539
- [9] Toner A and Hibbert A 2005 *Mon. Not. R. Astron. Soc.* **364** 683
- [10] Sugar J and Corliss C 1985 *J. Phys. Chem. Ref. Data* **14**, Suppl. 2
- [11] Nahar S N and Pradhan A K 1996 *Astron. Astrophys. Suppl. Ser.* **119** 569
- [12] Beck D R, programs REDUCE, RCI, RFV1S, unpublished
- [13] Desclaux J P 1975 *Comput. Phys. Commun.* **9** 31
- [14] Oksuz I and Sinanoglu O 1969 *Phys. Rev.* **181** 54
- [15] Beck D R and Nicolaides C A in *Excited States in Quantum Chemistry* 1978 ed Nicolaides C A and Beck D R (Dordrecht: Reidel) p.105ff
- [16] Jankowski K, Malinowski P and Polasik M 1979 *J. Phys. B* **12** 345
- [17] Weber J, Lacroix R, and Wanner G 1980 *Comp. Chem.* **4** 55
- [18] Nicolaides C A and Beck D R 1978 *Chem. Phys. Lett.* **53** 87
- [19] Nicolaides C A and Beck D R 1975 *Can. J. Phys.* **53** 1224

**Tables and table captions**

**Table 1.** Fe III  $3d^5 4p J=3$  energy levels (in  $\text{cm}^{-1}$ ) referenced to  $z^7P$  at  $82334 \text{ cm}^{-1}$ 

Label	Energy ( $\text{cm}^{-1}$ )		Adj. dE <sup>a</sup>		Landé $g$	Add Label <sup>c</sup>
	Expt <sup>b</sup>	RCI	Expt	RCI	RCI	
(a <sup>6</sup> S) z <sup>7</sup> P	0.	0.	0.	0.	1.914	99%
(a <sup>6</sup> S) z <sup>5</sup> P	6751.	6798.	6751.	6798.	1.667	98%
(a <sup>4</sup> G) z <sup>5</sup> G	31271.	32593.	24520.	25795.	0.904	93%
(a <sup>4</sup> G) z <sup>5</sup> H	32615.	33697.	1344.	1104.	0.517	96%
(a <sup>4</sup> P) z <sup>5</sup> D	34141.	35630.	1526.	1933.	1.363	35%; 41%( <sup>4</sup> G) <sup>5</sup> F
(a <sup>4</sup> G) z <sup>5</sup> F	34735.	36188.	594.	558.	1.382	46%; 40%( <sup>4</sup> P) <sup>5</sup> D
(a <sup>4</sup> G) z <sup>3</sup> F	35912.	37426.	1177.	1237.	1.094	89%
(a <sup>4</sup> P) y <sup>5</sup> P	36109.	37633.	197.	208.	1.646	63%; 28%( <sup>4</sup> D) <sup>5</sup> P
(a <sup>4</sup> D) y <sup>5</sup> F	38675.	39871.	2566.	2238.	1.256	84%
(a <sup>4</sup> G) z <sup>3</sup> G	39586.	40978.	911.	1107.	0.751	95%
(a <sup>4</sup> P) z <sup>3</sup> D	40013.	41318.	427.	340.	1.363	67%; 17%( <sup>2</sup> F) <sup>3</sup> D
(a <sup>4</sup> D) y <sup>5</sup> D	40496.	41695.	483.	377.	1.536	31%; 32%( <sup>4</sup> D) <sup>5</sup> P; 14%( <sup>4</sup> P) <sup>3</sup> D
(a <sup>4</sup> D) x <sup>5</sup> P	41416.	42584.	920.	889.	1.570	33%; 32%( <sup>4</sup> D) <sup>5</sup> D; 19%( <sup>4</sup> P) <sup>5</sup> P
(a <sup>4</sup> D) y <sup>3</sup> D	42520.	43942.	1104.	1358.	1.339	79%
(a <sup>4</sup> D) y <sup>3</sup> F	43304.	44525.	784.	583.	1.104	85%
(a <sup>2</sup> D) x <sup>3</sup> F	49746.	51663.	6442.	7137.	1.068	59%; 26%( <sup>2</sup> F) <sup>3</sup> F
(a <sup>2</sup> F) y <sup>3</sup> G	52215.	54088.	2469.	2426.	0.900	44%; 35%( <sup>2</sup> D) <sup>1</sup> F
(a <sup>2</sup> D) x <sup>3</sup> D	52642.	54318.	427.	229.	1.162	49%; 31%( <sup>4</sup> F) <sup>5</sup> G
(a <sup>4</sup> F) y <sup>5</sup> G	52762.	54471.	120.	154.	1.045	54%; 24%( <sup>2</sup> D) <sup>3</sup> D
(a <sup>2</sup> F) w <sup>3</sup> D	53372.	55139.	610.	668.	1.311	88%
(a <sup>4</sup> F) x <sup>5</sup> F	53675.	55450.	303.	311.	1.266	77%; 10%( <sup>4</sup> F) <sup>5</sup> D
(a <sup>2</sup> D) z <sup>1</sup> F	53866.	55623.	191.	173.	0.916	26%; 38%( <sup>2</sup> F) <sup>3</sup> G
(a <sup>2</sup> F) w <sup>3</sup> F	54463.	56213.	597.	590.	1.095	44%; 16%( <sup>2</sup> D) <sup>3</sup> F
(a <sup>4</sup> F) x <sup>5</sup> D	55089.	56894.	626.	681.	1.461	81%
(a <sup>2</sup> H) x <sup>3</sup> G	55853.	57931.	764.	1037.	0.763	25%; 55%( <sup>4</sup> F) <sup>3</sup> G
(a <sup>4</sup> F) w <sup>3</sup> G	57346.	59520.	1493.	1589.	0.776	17%; 48%( <sup>2</sup> G) <sup>3</sup> G; 20%( <sup>2</sup> H) <sup>3</sup> H
(a <sup>2</sup> F) y <sup>1</sup> F	58119.	60235.	773.	715.	0.999	55%
(a <sup>2</sup> G) v <sup>3</sup> F	58359.	60402.	240.	168.	1.119	29%; 25%( <sup>4</sup> F) <sup>3</sup> F; 17%( <sup>4</sup> F) <sup>3</sup> D
(a <sup>4</sup> F) v <sup>3</sup> D	59133.	61006.	774.	603.	1.272	63%
(a <sup>4</sup> F) u <sup>3</sup> F	59979.	62077.	846.	1071.	1.078	41%; 29%( <sup>2</sup> G) <sup>3</sup> F; 23%( <sup>2</sup> F) <sup>3</sup> F
(a <sup>2</sup> G) v <sup>3</sup> G	61783.	63692.	1804.	1615.	0.767	41%; 26%( <sup>2</sup> F) <sup>3</sup> G; 18%( <sup>4</sup> F) <sup>3</sup> G
(b <sup>2</sup> F) t <sup>3</sup> F	62237.	64195.	454.	503.	1.076	72%; 13%( <sup>2</sup> G) <sup>3</sup> F
(a <sup>2</sup> G) x <sup>1</sup> F	62705.	65022.	468.	827.	0.999	79%
(b <sup>2</sup> F) u <sup>3</sup> G	64557.	66372.	1852.	1350.	0.759	52%; 39%( <sup>2</sup> F) <sup>3</sup> G
(b <sup>2</sup> F) u <sup>3</sup> D	65302.	67020.	745.	649.	1.327	86%
(b <sup>2</sup> F) w <sup>1</sup> F	68321.	70308.	3019.	3288.	1.002	94%
(b <sup>2</sup> D) s <sup>3</sup> F	75648.	77871.	7327.	7562.	1.116	74%; 15%( <sup>2</sup> D) <sup>3</sup> D
(b <sup>2</sup> D) t <sup>3</sup> D	76395.	78543.	747.	672.	1.288	80%; 16%( <sup>2</sup> D) <sup>3</sup> F
(b <sup>2</sup> D) v <sup>1</sup> F	77159.	79486.	764.	942.	1.010	84%
(b <sup>2</sup> G) r <sup>3</sup> F	84164.	87129.	7005.	7644.	0.865	32%; 65%( <sup>2</sup> G) <sup>3</sup> G
(b <sup>2</sup> G) t <sup>3</sup> G	84751.	87706.	587.	577.	0.969	34%; 62%( <sup>2</sup> G) <sup>3</sup> G
(b <sup>2</sup> G) u <sup>1</sup> F	87977.	91143.	3226.	3437.	0.998	89%

<sup>a</sup>  $E_n - E_{n-1}$  for  $n$ th level

<sup>b</sup> From [10]

<sup>c</sup> The first number gives the percent weight of the lead term; the second (and following) gives the percent weight and label

**Table 2.** Fe III  $3d^5 4p J=4$  energy levels (in  $\text{cm}^{-1}$ ) referenced to  $z^7P$  at  $82847 \text{ cm}^{-1}$ 

Label	Energy ( $\text{cm}^{-1}$ )		Adj. dE <sup>a</sup>		Landé $g$	Add Label <sup>c</sup>
	Expt <sup>b</sup>	RCI	Expt	RCI	RCI	
(a <sup>6</sup> S) z <sup>7</sup> P	0.	0.	0.	0.	1.749	100%
(a <sup>4</sup> G) z <sup>5</sup> G	30788.	32033.	30788.	32033.	1.131	90%
(a <sup>4</sup> G) z <sup>5</sup> H	32264.	33310.	1476.	1277.	0.921	90%
(a <sup>4</sup> G) z <sup>5</sup> F	33620.	35049.	1356.	1739.	1.352	77%
(a <sup>4</sup> P) z <sup>5</sup> D	34675.	35934.	1055.	885.	1.483	75%
(a <sup>4</sup> G) z <sup>3</sup> F	35503.	36408.	828.	474.	1.253	89%
(a <sup>4</sup> G) z <sup>3</sup> H	35839.	36817.	336.	408.	0.802	96%
(a <sup>4</sup> D) y <sup>5</sup> F	38395.	39469.	2556.	2653.	1.352	87%
(a <sup>4</sup> G) z <sup>3</sup> G	39094.	40267.	699.	798.	1.051	94%
(a <sup>4</sup> D) y <sup>5</sup> D	40097.	41174.	1003.	907.	1.491	79%; 15%( <sup>4</sup> P) <sup>5</sup> D
(a <sup>4</sup> D) y <sup>3</sup> F	42597.	43557.	2500.	2383.	1.258	87%
(a <sup>2</sup> I) y <sup>3</sup> H	49812.	51293.	7215.	7736.	0.809	89%
(a <sup>2</sup> D) x <sup>3</sup> F	49938.	51388.	126.	95.	1.222	61%; 25%( <sup>2</sup> F) <sup>3</sup> F
(a <sup>2</sup> F) z <sup>1</sup> G	51513.	52973.	1575.	1586.	1.020	54%; 18%( <sup>2</sup> F) <sup>3</sup> G
(a <sup>4</sup> F) y <sup>5</sup> G	52393.	53821.	880.	848.	1.130	75%
(a <sup>2</sup> F) y <sup>3</sup> G	52707.	53966.	314.	145.	1.124	50%; 31%( <sup>2</sup> F) <sup>3</sup> F
(a <sup>4</sup> F) x <sup>5</sup> F	53144.	54614.	437.	647.	1.354	78%
(a <sup>2</sup> F) w <sup>3</sup> F	53766.	55053.	622.	440.	1.197	35%; 33%( <sup>2</sup> D) <sup>3</sup> F
(a <sup>4</sup> F) x <sup>5</sup> D	54363.	55850.	597.	796.	1.468	79%
(a <sup>2</sup> G) x <sup>3</sup> H	54681.	56041.	318.	191.	0.822	53%; 34%( <sup>2</sup> H) <sup>3</sup> H
(a <sup>2</sup> H) x <sup>3</sup> G	55256.	56670.	575.	629.	1.046	28%; 50%( <sup>4</sup> F) <sup>3</sup> G
(a <sup>4</sup> F) w <sup>3</sup> G	56778.	58158.	1522.	1488.	1.110	0%; 28%( <sup>2</sup> G) <sup>1</sup> G; 27%( <sup>2</sup> G) <sup>3</sup> F
(a <sup>2</sup> G) y <sup>1</sup> G	56980.	58216.	202.	58.	1.053	0%; 42%( <sup>2</sup> G) <sup>3</sup> G; 24%( <sup>4</sup> F) <sup>3</sup> G
(a <sup>2</sup> G) v <sup>3</sup> F	58156.	59164.	1176.	948.	1.133	39%; 27%( <sup>2</sup> G) <sup>1</sup> G
(a <sup>4</sup> F) u <sup>3</sup> F	59200.	60634.	1044.	1470.	1.245	63%; 20%( <sup>2</sup> F) <sup>3</sup> F
(a <sup>2</sup> H) w <sup>3</sup> H	60009.	61167.	809.	533.	0.818	58%; 32%( <sup>2</sup> G) <sup>3</sup> H
(a <sup>2</sup> G) v <sup>3</sup> G	61239.	62351.	1230.	1184.	1.047	41%; 25%( <sup>2</sup> F) <sup>3</sup> G
(b <sup>2</sup> F) t <sup>3</sup> F	61485.	62911.	246.	560.	1.124	40%; 28%( <sup>2</sup> F) <sup>1</sup> G
(a <sup>2</sup> H) x <sup>1</sup> G	62122.	63514.	637.	603.	1.121	12%; 39%( <sup>2</sup> F) <sup>3</sup> F; 29%( <sup>2</sup> F) <sup>1</sup> G
(b <sup>2</sup> F) u <sup>3</sup> G	64314.	65283.	2192.	1769.	1.052	57%; 34%( <sup>2</sup> H) <sup>3</sup> G
(b <sup>2</sup> F) w <sup>1</sup> G	66166.	67242.	1852.	1959.	1.001	44%; 26%( <sup>2</sup> H) <sup>1</sup> G; 19%( <sup>2</sup> G) <sup>1</sup> G
(b <sup>2</sup> D) s <sup>3</sup> F	75716.	77265.	9550.	10022.	1.249	94%
(b <sup>2</sup> G) v <sup>3</sup> H	82872.	84093.	7156.	6828.	0.805	97%
(b <sup>2</sup> G) r <sup>3</sup> F	83375.	84710.	503.	617.	1.239	90%
(a <sup>6</sup> S) y <sup>7</sup> P	83574.	85228.	199.	519.	1.749	100% $3d^5 5p$
(b <sup>2</sup> G) t <sup>3</sup> G	84360.	85995.	786.	767.	1.053	94%
(b <sup>2</sup> G) v <sup>1</sup> G	86431.	87739.	2071.	1744.	1.001	96%

<sup>a</sup>  $E_n - E_{n-1}$  for  $n$ th level

<sup>b</sup> From [10]

<sup>c</sup> The first number gives the percent weight of the lead term; the second (etc.) gives the percent weight and label

**Table 3.** Fe III  $3d^5 4p J=5$  energy levels (in  $\text{cm}^{-1}$ ) referenced to  $z^5G$  at  $113677 \text{ cm}^{-1}$ 

Label	Energy ( $\text{cm}^{-1}$ )		Adj. dE <sup>a</sup>		Landé $g$	Add Label <sup>c</sup>
	Expt <sup>b</sup>	RCI	Expt	RCI	RCI	
(a <sup>4</sup> G) z <sup>5</sup> G	0.	0.	0.	0.	1.256	91%
(a <sup>4</sup> G) z <sup>5</sup> H	1613.	1505.	1613.	1505.	1.110	93%
(a <sup>4</sup> G) z <sup>5</sup> F	2640.	2783.	1027.	1277.	1.397	90%
(a <sup>4</sup> G) z <sup>3</sup> H	4880.	4802.	2240.	2019.	1.034	96%
(a <sup>4</sup> D) y <sup>5</sup> F	7792.	7648.	2912.	2846.	1.399	92%
(a <sup>4</sup> G) z <sup>3</sup> G	8273.	8108.	481.	459.	1.201	95%
(a <sup>2</sup> I) z <sup>3</sup> I	16579.	16551.	8306.	8444.	0.861	81%
(a <sup>2</sup> I) z <sup>1</sup> H	18034.	18149.	1455.	1598.	0.979	70%; 14%( <sup>2</sup> I) <sup>3</sup> I
(a <sup>2</sup> I) y <sup>3</sup> H	18888.	19035.	854.	886.	1.030	87%
(a <sup>4</sup> F) y <sup>5</sup> G	21639.	21587.	2751.	2552.	1.254	64%; 20%( <sup>2</sup> F) <sup>3</sup> G
(a <sup>2</sup> F) y <sup>3</sup> G	22059.	22070.	420.	483.	1.229	62%; 29%( <sup>4</sup> F) <sup>5</sup> G
(a <sup>4</sup> F) x <sup>5</sup> F	22508.	22399.	449.	329.	1.367	79%; 13%( <sup>2</sup> F) <sup>3</sup> G
(a <sup>2</sup> G) x <sup>3</sup> H	24087.	24232.	1579.	1833.	1.037	40%; 40%( <sup>2</sup> H) <sup>3</sup> H
(a <sup>2</sup> H) x <sup>3</sup> G	24378.	24585.	291.	353.	1.196	41%; 39%( <sup>4</sup> F) <sup>3</sup> G
(a <sup>4</sup> F) w <sup>3</sup> G	25786.	25754.	1408.	1169.	1.046	19%; 42%( <sup>2</sup> H) <sup>3</sup> I; 25%( <sup>2</sup> G) <sup>3</sup> G
(a <sup>2</sup> H) y <sup>3</sup> I	25832.	25809.	46.	55.	0.997	46%; 13%( <sup>4</sup> F) <sup>3</sup> G; 13%( <sup>2</sup> G) <sup>3</sup> G
(a <sup>2</sup> H) w <sup>3</sup> H	29231.	29041.	3399.	3232.	1.051	39%; 45%( <sup>2</sup> G) <sup>3</sup> H
(a <sup>2</sup> G) v <sup>3</sup> G	30207.	30001.	976.	960.	1.171	36%; 16%( <sup>2</sup> H) <sup>3</sup> G, <sup>3</sup> I/( <sup>4</sup> F) <sup>3</sup> G
(a <sup>2</sup> G) y <sup>1</sup> H	30910.	30662.	703.	661.	1.005	59%; 33%( <sup>2</sup> H) <sup>1</sup> H
(a <sup>2</sup> H) x <sup>1</sup> H	31166.	31148.	256.	486.	1.006	56%; 28%( <sup>2</sup> G) <sup>1</sup> H; 12%( <sup>2</sup> I) <sup>1</sup> H
(b <sup>2</sup> F) u <sup>3</sup> G	33729.	33540.	2563.	2392.	1.199	71%; 25%( <sup>2</sup> H) <sup>3</sup> G
(b <sup>2</sup> G) v <sup>3</sup> H	52263.	52821.	18534.	19281.	1.062	78%; 18%( <sup>2</sup> G) <sup>3</sup> G
(b <sup>2</sup> G) t <sup>3</sup> G	53622.	53749.	1359.	928.	1.167	80%; 19%( <sup>2</sup> G) <sup>3</sup> H
(b <sup>2</sup> G) w <sup>1</sup> H	55103.	55584.	1481.	1835.	1.003	95%

<sup>a</sup>  $E_n - E_{n-1}$  for  $n$ th level

<sup>b</sup> From [10]

<sup>c</sup> The first number gives the percent weight of the lead term; the second (etc. ) gives the percent weight and label

**Table 4.** Fe III  $3d^6 J=4 \rightarrow 3d^5 4p J=3$  RCI  $f$ -values using experimental dE [10]; only values  $> 0.01$  shown. The “spread” is defined by  $|f_t - f_v|/f_{avg} \times 50$ .

Label <sup>a</sup>	RCI			Semi-Empirical		
	Vel	Len	Spread <sup>b</sup>	K <sup>c</sup>	R <sup>d</sup>	E <sup>e</sup>
a $^5D \rightarrow (a \ ^6S)$ z $^5P$	.0586	.0622	3.1%	.0776	.0544	.0537
a $^5D \rightarrow (a \ ^4P)$ y $^5P$	.0617	.0602	1.2%	.0652	.0715	.0180
a $^3H \rightarrow (a \ ^4G)$ z $^3G$	.0575	.0605	2.5%	.0798	.0630	.0630
a $^3H \rightarrow (a \ ^2F)$ y $^3G$	.0103	.0105	1.3%	.0152	.0107	.0142
a $^3H \rightarrow (a \ ^4F)$ w $^3G$	.0209	.0216	1.6%	.0269	.0278	.0224
a $^3H \rightarrow (a \ ^2G)$ v $^3G$	.0431	.0435	0.5%	.0586	.0524	.0517
a $^3F \rightarrow (a \ ^4P)$ z $^3D$	.0188	.0197	2.4%	.0227	.0234	.0140
a $^3F \rightarrow (a \ ^4D)$ y $^3D$	.0198	.0200	0.5%	.0274	.0213	.0203
a $^3F \rightarrow (a \ ^2D)$ x $^3D$	.0413	.0408	0.7%	.0588	.0466	.0547
a $^3F \rightarrow (a \ ^4F)$ y $^5G$	.0165	.0163	0.4%	.0198	.0233	.0101
a $^3G \rightarrow (a \ ^4D)$ y $^3F$	.0411	.0422	1.4%	.0527	.0411	.0412
a $^3G \rightarrow (a \ ^2F)$ w $^3F$	.0170	.0175	1.4%	.0238	.0212	.0174
a $^3G \rightarrow (a \ ^4F)$ u $^3F$	.0415	.0424	1.1%	.0548	.0482	.0491
a $^1G \rightarrow (a \ ^2F)$ y $^1F$	.0576	.0587	1.0%	.0904	.0655	.0806
a $^1G \rightarrow (a \ ^2G)$ v $^3F$	.0153	.0157	1.1%	.0129	.0254	.0030
a $^1G \rightarrow (a \ ^4F)$ v $^3D$	.0100	.0103	1.3%	.0100	.0101	.0077
a $^1G \rightarrow (a \ ^2G)$ x $^1F$	.0438	.0436	0.2%	.0552	.0478	.0456
a $^1G \rightarrow (b \ ^2F)$ w $^1F$	.0218	.0229	2.5%	.0307	.0251	.0269
b $^3F \rightarrow (a \ ^4F)$ v $^3D$	.0267	.0282	2.8%	.0390	.0250	.0250
b $^3F \rightarrow (a \ ^2P)$ s $^3D$	.0377	.0370	0.9%			
b $^1G \rightarrow (b \ ^2F)$ w $^1F$	.0164	.0166	0.7%	.0236	.0194	.0195
b $^1G \rightarrow (b \ ^2D)$ v $^1F$	.0168	.0173	1.3%	.0191	.0144	.0139
b $^1G \rightarrow (b \ ^2G)$ u $^1F$	.0642	.0642	0.0%	.0887	.0833	.0810

<sup>a</sup> Labels are from ref.[10]; Differences with RCI labels are discussed in the text.

<sup>b</sup> The average spread is 0.8%

<sup>c</sup> Kurucz [6]

<sup>d</sup> Raassen [7]

<sup>e</sup> Ekberg [5]

**Table 5.** Fe III  $3d^6$   $J=4 \rightarrow 3d^5 4p$   $J=4$  RCI  $f$ -values using experimental dE [10]; only values  $> 0.01$  shown. The “spread” is defined by  $|f_t - f_v|/f_{avg} \times 50$ .

Label <sup>a</sup>	RCI			Semi-Empirical		
	Vel	Len	Spread <sup>b</sup>	K <sup>c</sup>	R <sup>d</sup>	E <sup>e</sup>
a $^5D \rightarrow (a \ ^4G)$ z $^5F$	.0147	.0135	4.0%	.0050	.0183	.0176
a $^5D \rightarrow (a \ ^4D)$ y $^5D$	.0559	.0537	2.0%	.0710	.0687	.0638
a $^5D \rightarrow (a \ ^4F)$ x $^5D$	.0372	.0355	2.3%	.0401	.0424	.0403
a $^3H \rightarrow (a \ ^4G)$ z $^3H$	.0277	.0289	2.1%	.0284	.0289	.0294
a $^3H \rightarrow (a \ ^2I)$ y $^3H$	.0528	.0524	0.4%	.0783	.0704	.0694
a $^3H \rightarrow (a \ ^2G)$ x $^3H$	.0322	.0323	0.2%	.0456	.0438	.0383
a $^3H \rightarrow (a \ ^2H)$ w $^3H$	.0147	.0145	0.7%	.0133	.0124	.0112
a $^3F \rightarrow (a \ ^4G)$ z $^3F$	.0304	.0301	0.4%	.0415	.0322	.0321
a $^3F \rightarrow (a \ ^2F)$ y $^3G$	.0088	.0086	0.8%	.0121	.0133	.0118
a $^3F \rightarrow (a \ ^2F)$ w $^3F$	.0139	.0142	0.9%	.0221	.0174	.0175
a $^3F \rightarrow (a \ ^4F)$ w $^3G$	.0210	.0204	1.1%	<.001	<.001	
a $^3F \rightarrow (a \ ^2G)$ y $^1G$	.0017	.0015	4.8%	.0134	.0169	.0098
a $^3F \rightarrow (a \ ^2G)$ v $^3F$	.0196	.0190	1.4%	.0346	.0314	.0319
a $^3G \rightarrow (a \ ^4G)$ z $^3G$	.0214	.0229	3.2%	.0284	.0201	.0225
a $^3G \rightarrow (a \ ^2H)$ x $^3G$	.0289	.0293	0.7%	.0545	.0484	.0511
a $^3G \rightarrow (a \ ^4F)$ w $^3G$	.0039	.0039	0.0%	.0148	.0160	.0103
a $^3G \rightarrow (a \ ^2G)$ y $^1G$	.0215	.0202	3.0%	.0010	.0012	.0010
a $^3G \rightarrow (a \ ^2G)$ v $^3G$	.0214	.0210	1.0%	.0283	.0270	.0228
a $^1G \rightarrow (a \ ^4F)$ w $^3G$	.0355	.0353	0.2%	.0012	<.001	.0019
a $^1G \rightarrow (a \ ^2G)$ y $^1G$	.0013	.0013	0.3%	.0780	.0651	.0684
a $^1G \rightarrow (a \ ^2G)$ v $^3F$	.0371	.0367	0.5%	.0267	.0319	.0180
a $^1G \rightarrow (b \ ^2F)$ t $^3F$	.0216	.0214	0.5%	.0247	.0187	.0263
a $^1G \rightarrow (a \ ^2H)$ x $^1G$	.0272	.0269	0.7%	.0209	.0183	.0151
b $^3F \rightarrow (a \ ^4F)$ u $^3F$	.0520	.0536	1.5%	.0641	.0474	.0498
b $^3F \rightarrow (b \ ^2F)$ t $^3F$	.0104	.0110	2.7%	.0110	.0101	.0064
b $^3F \rightarrow (b \ ^2G)$ r $^3F$	.0618	.0595	1.9%	.0705	.0674	.0641
b $^1G \rightarrow (b \ ^2F)$ w $^1G$	.0412	.0446	4.0%	.0560	.0443	.0417
b $^1G \rightarrow (b \ ^2G)$ v $^1G$	.0942	.0934	0.4%	.1191	.1030	.1007

<sup>a</sup> Labels are from ref.[10]; Differences with RCI labels are discussed in the text.

<sup>b</sup> The average spread is 1.5%

<sup>c</sup> Kurucz [6]

<sup>d</sup> Raassen [7]

<sup>e</sup> Ekberg [5]

**Table 6.** Fe III  $3d^6 J=4 \rightarrow 3d^5 4p J=5$  RCI  $f$ -values using experimental dE [10]; only values  $> 0.01$  shown. The “spread” is defined by  $|f_t - f_v|/f_{avg} \times 50$ .

Label <sup>a</sup>	RCI			Semi-Empirical		
	Vel	Len	Spread <sup>b</sup>	K <sup>c</sup>	R <sup>d</sup>	E <sup>e</sup>
a $^5D \rightarrow (a \ ^4G) z \ ^5F$	.1031	.0957	3.7%	.1253	.1192	.1149
a $^5D \rightarrow (a \ ^4D) y \ ^5F$	.0134	.0126	3.0%	.0159	.0144	.0156
a $^5D \rightarrow (a \ ^4F) x \ ^5F$	.0130	.0111	7.9%	.0152	.0164	.0165
a $^3H \rightarrow (a \ ^2I) z \ ^3I$	.0369	.0342	3.8%	.0447	.0392	.0391
a $^3F \rightarrow (a \ ^4G) z \ ^3G$	.0248	.0248	0.1%	.0328	.0272	.0254
a $^3F \rightarrow (a \ ^2H) x \ ^3G$	.0235	.0206	6.7%	.0394	.0346	.0382
a $^3F \rightarrow (a \ ^4F) w \ ^3G$	.0247	.0226	4.4%	.0308	.0322	.0194
a $^3F \rightarrow (a \ ^2H) y \ ^3I$	.0088	.0081	4.1%	<.001	<.001	
a $^3G \rightarrow (a \ ^4G) z \ ^3H$	.0122	.0114	3.3%	.0141	.0126	.0097
a $^3G \rightarrow (a \ ^2I) y \ ^3H$	.0368	.0339	4.0%	.0441	.0403	.0374
a $^3G \rightarrow (a \ ^2H) w \ ^3H$	.0165	.0159	1.8%	.0207	.0205	.0182
a $^3G \rightarrow (a \ ^2G) v \ ^3G$	.0086	.0084	1.2%	.0105	.0074	.0105
a $^1G \rightarrow (a \ ^2I) z \ ^1H$	.0440	.0405	4.1%	.0521	.0445	.0408
a $^1G \rightarrow (a \ ^2G) y \ ^1H$	.0248	.0244	0.9%	.0122	.0170	.0012
b $^3F \rightarrow (a \ ^2G) v \ ^3G$	.0167	.0165	0.7%	.0182	.0130	.0116
b $^3F \rightarrow (b \ ^2F) u \ ^3G$	.0123	.0125	0.7%	.0179	.0146	.0138
b $^3F \rightarrow (b \ ^2G) v \ ^3H$	.0065	.0061	3.2%	.0033	.0031	.0029
b $^3F \rightarrow (b \ ^2G) t \ ^3G$	.0273	.0253	3.7%	.0377	.0344	.0336
b $^1G \rightarrow (a \ ^2G) y \ ^1H$	.0048	.0045	3.2%	.0066	<.001	
b $^1G \rightarrow (a \ ^2H) x \ ^1H$	.0406	.0382	3.0%	.0502	.0416	.0171
b $^1G \rightarrow (b \ ^2G) w \ ^1H$	.0154	.0155	0.1%	.0200	.0175	.0165

<sup>a</sup> Labels are from ref.[10]; Differences with RCI labels are discussed in the text.

<sup>b</sup> The average spread is 3.0%

<sup>c</sup> Kurucz [6]

<sup>d</sup> Raassen [7]

<sup>e</sup> Ekberg [5]